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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to Fuel Cells

We, "SHELL" RESEARCH LIMITED, a British company, of Shell Centre, London, S.E.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fuel cells and is particularly concerned with high temperature fuel cells which comprise solid state oxide electrolytes wherein conduction of electricity through the electrolyte is via transport of anion only, that is to say electrons are transferred from the oxidant electrode by oxygen ions to the fuel electrode, discharged thereat and returned to the oxidant electrode via an external circuit.

In certain solid state oxides oxygen appears to migrate through the crystal lattice via oxygen ion vacancies in said lattice, i.e. such materials conduct electricity by anion transport only. An example is the mixed oxide of zirconia and lime which crystallises in an imperfect fluorite type of lattice, has the atomic ratios of $Zr_{0.85}Ca_{0.15}O_{1.15}$ and is believed to maintain the fluorite type of lattice because it contains oxygen ion vacancies generated by the replacement of zirconium atoms by calcium atoms in the ratio indicated above; these vacancies, which promote transfer of the anion O^{2-} through the lattice, are postulated to arise because, for valency reasons, each calcium atom combines with only one oxygen atom instead of two required by zirconium.

Other combinations of oxides which give crystal lattices having therein oxygen ion vacancies are known; for example oxygen ion vacancies can be generated in the crystal lattice of the oxides of hafnium and thorium by oxides of such elements as calcium, lanthanum and yttrium.

Particular advantages offered by a solid state electrolyte are that a fuel cell comprising such electrolyte can successfully utilise, inter alia, gaseous hydrocarbon fuels and is free of

the disadvantages inherent in the liquid electrolyte or molten electrolyte type of fuel cell. However, the development of fuel cells utilising as electrolytes solid state oxides wherein electrical conduction is by anion transport only has hitherto been impeded by the difficulty of constructing and supporting thin layers of the solid state electrolyte, said thin layers being essential in order to achieve current densities of practical value at temperatures which are convenient to induce and maintain and which do not promote oxidative attack on the fuel cell components.

It has now been found that thin, solid state oxide electrolyte films can be made by plasma spraying the solid state electrolyte on to a porous metal substrate. It has further been found that if the porous metal substrate is first coated by flame spraying with a thin porous layer of nickel aluminide and then coated with the solid state electrolyte, the electrolyte/substrate bond is greatly strengthened and furthermore catalytic activity at the substrate/electrolyte junction is improved. The catalytic activity can be further enhanced by adding to the layer of nickel aluminide a thin layer of platinum, palladium, iridium, ruthenium or rhodium. It has also been found that if the free face of an electrolyte layer deposited on a porous metal substrate is subsequently coated with a thin conductive layer there is produced a fuel cell unit wherein the porous metal substrate forms the fuel electrode, the thin conductive layer forms the oxidant electrode and the solid state oxide forms the electrolyte and wherein said electrodes are intimately bonded to said electrolyte.

Accordingly one aspect of the present invention comprises a fuel cell unit said unit comprising a porous metal substrate having applied to one surface thereof a porous layer of nickel aluminide followed by a layer of solid oxide electrolyte as herein defined and then by an oxygen permeable layer of conductive material,

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A porous layer of platinum, palladium, iridium, ruthenium or rhodium may with advantage be applied to the layer of nickel aluminide.

Another aspect of the present invention comprises a method of constructing a fuel cell unit said method comprising flame spraying a layer of nickel aluminide on to a porous metal substrate, plasma spraying a layer of solid oxide electrolyte as herein defined on to said layer of nickel aluminide and thereafter coating said oxide layer with a layer of conductive material.

It will be appreciated that fuel cell units according to the present invention can be connected together by various means to form a battery and accordingly the present invention includes as a further aspect a fuel cell comprising a plurality of fuel cell units as hereinbefore described.

The porous metal substrate may take the form of a disc or sheet of metal having catalytic properties with respect to the fuel to be used and being so fabricated as to have an average pore diameter within the range 0.1 to 500 microns and preferably within the range 1 to 100 microns. In the specification the term "average pore diameter" refers to a specific property of the substrate, which can be ascertained by measuring the pressure necessary to force air, applied over the surface of the porous substrate, through the pores when the substrate is thoroughly wetted by a suitable liquid. The average pore diameter d is then defined by the equation

$$d = 4T$$

—
p

where p is the pressure in dynes/cm.² and T is the surface tension of the liquid in dynes/cm. Stainless steel and nickel are suitable materials. The thickness of the porous metal substrate may be in the range 0.001" to 0.1"; a thickness within the range 0.01" to 0.05" is preferred but the thickness chosen will depend essentially upon the size of the fuel cell unit to be constructed.

The porous film of nickel aluminide is best applied by the flame spraying process known under the trade name "Metco 404 Process." Film thicknesses in the range 0.0005 to 0.05" are desirable but it is preferred to establish films having thicknesses within the range 0.002" to 0.02". As hereinbefore mentioned, the nickel aluminide film in addition to strengthening the bond between the solid state electrolyte and the porous metal substrate enhances the catalytic activity of said substrate with respect to the fuel to be used. This catalytic activity may be further enhanced by treatment of the flame sprayed coating of nickel aluminide with an aqueous alkali, e.g., 6N KOH, before the zirconia is applied, but

is preferably enhanced by applying to the free surface of the nickel aluminide a thin layer of platinum, palladium, iridium, ruthenium or rhodium, e.g. a platinum paint of the kind marketed under the Trade Name "Johnson & Matther Bright Platinum G."

In this specification the term "solid state oxide" means an oxide which conducts electricity by an anion transfer process and which does not become unduly electronically conductive (or semi-conductive) in a normal sense at elevated temperatures. Subject thereto, oxides which crystallise in the fluorite type of lattice are generally suitable. For example, oxides of zirconium, hafnium and thorium and mixtures thereof, mixed with oxides of other metals of lower valency for example, calcium, and certain rare earths, e.g. lanthanum, yttrium, and scandium, chosen and supplied in such proportions as to maintain a fluorite type of crystal lattice, are suitable. Particularly suitable are oxides of zirconium, stabilised with lime or yttria, especially oxides of zirconium stabilised with amounts of lime in the range 10—15 mole % or yttria in the range 5—12 mole %, e.g. oxides having the atomic ratios $Zr_{0.9}Ca_{0.1}O_{1.9}$ or $Zr_{0.92}Y_{0.18}O_{2.08}$. The oxide layer is applied to the nickel aluminide layer by means of the plasma spray process, i.e. a process in which a mixture of zirconium oxide and lime or yttria particles is passed through an arc struck in a current of nitrogen and hydrogen, the gas temperature of which is raised to a value exceeding the melting point of zirconia, so that molten oxide particles are projected against a receiving surface. Oxide film thickness within the range 0.0001" to 0.1" are useful; film thicknesses within the range 0.0005 to 0.05" are desirable while film thicknesses within the range 0.001 to 0.01" are especially preferred.

The conductive layer applied to the electrolyte film may comprise metals from Group 1B of the Periodic Table or platinum, palladium, iridium, ruthenium or rhodium or mixtures thereof but silver is preferred on grounds of catalytic activity, conductivity, ease of application and cheapness. In general the conductive film should be porous in nature and may be applied to the electrolyte film by flame spraying, chemical reduction methods or vacuum evaporation and if desired may be thickened by electrodeposition. If the conductive layer is to be applied by flame spraying, it is desirable to incorporate an inorganic support for the metal, i.e. to spray the metal admixed with, for example, oxides of such metals as zirconium, zinc or aluminium. If silver or alloys comprising substantial amounts of silver are used then a porous film is not essential because oxygen can pass through the silver layer by dissolution. Suitable thicknesses for the conductive layer are thicknesses within the range 0.03 microns—50 microns if the film is

substantially continuous, while greater thicknesses, e.g. up to 200 microns are useful if the film is porous.

Fuel cell units of the present invention are capable of operating on a wide range of fuels, for example hydrogen, carbon monoxide, water gas, producer gas, hydrocarbon gases, e.g. methane, ethane and propane, and mixtures thereof, and such materials as methyl alcohol and ethyl alcohol when supplied in vapour form. It is advantageous when utilizing hydrocarbon fuels to supply the hydrocarbon admixed with steam; one way of doing this is to supply the hydrocarbon fuel admixed with the exhaust gas obtained from the fuel electrode side of the cell.

Since a fuel cell unit as herein described is a simple thin, compact but relatively robust structure it can conveniently be mounted between end plates e.g. stainless steel end plates, so as to enclose gas spaces, thereby forming a fuel cell comprising a single fuel cell unit. Alternatively a battery may be formed by mounting a plurality of fuel cell units between electrically insulating, gas impervious spacers so that electrodes of like polarity enclose alternatively oxidant and fuel gas or fuel gas and oxidant spaces, such assembly being mounted between end plates. A further arrangement is to mount a plurality of fuel cell units according to the present invention such that electrodes of unlike polarity face each other and to provide gas impervious partitions to divide the gas space so formed between the units into oxidant and fuel gas spaces, the fuel cell units being separated from the partitions by means of suitable gas impervious spacers.

When starting a fuel cell unit according to the present invention it is first necessary to heat the electrolyte. This may be effected in a variety of ways, e.g. by the provision of electrical heaters integral with each unit or with the battery as a whole or by supplying hot gases to the fuel cell assembly or by supplying heat in any other convenient manner. However, when a battery of such fuel cell units is supplying current at high output, it will generally be that the electrochemical reactions responsible for the generation of electricity will supply the heat necessary for maintaining the temperature at a suitable level and the external heat supply may be discontinued.

An embodiment of the present invention will now be described with reference to the accompanying drawings wherein

Fig. 1 is a vertical central section of a fuel cell on a plane at right angles to the face of the porous metal substrate, and

Fig. 2 is a plan view of the inner face of an end plate of the fuel cell.

Referring to Fig. 1 a fuel cell has end plates 1 and 2, between which and separated therefrom by silver gaskets 3 and 4 is a fuel cell unit consisting of a porous metal substrate 5, a layer of nickel aluminide 6, a solid oxide

electrolyte 7 and a layer of conductive material 8. The end plate 1, gasket 3 and porous metal substrate 5 enclose a fuel space 9. The end plate 2, gasket 4 and conductive layer 8 enclose an oxidant space 10. The end plate 1 is provided with a fuel entry conduit 11 and a fuel exit conduit 12. An annular projection 13 mounted on the fuel space side of end plate 1 and formed with an aperture 14 gives access to the fuel exit conduit 12. The end plate 2 is provided with an oxidant entry conduit 15 and an oxidant exit conduit 16; an annular projection 17 mounted on the oxidant space side of the end plate 2 and formed with an aperture 18 gives access to the oxidant exit conduit 16. The fuel cell is held together by brackets 19 and 20 through which pass retaining bolts 21 and 22 and the end plate 1 is electrically insulated from the bracket 19 by an insulating gasket 23. Electrical continuity between the fuel cell and apparatus absorbing the electrical output developed when the fuel cell is in operation is maintained by leads (not shown) suitably attached to the end plates 1 and 2.

In operation, the fuel cell is first brought to operating temperature by preheating in an electric furnace. Fuel is then supplied to the fuel space 9 via the fuel entry conduit 11 and unreacted fuel is withdrawn from the fuel space 9 via the exit conduit 12 after having circulated over the surface of the fuel electrode in the manner indicated by the broken arrows in the drawing of Fig. 2. Oxidant is supplied to the oxidant space 10 via the oxidant entry conduit 15 and unreacted oxidant withdrawn via the exit conduit 16, circulation of oxidant over the surface of the oxidant electrode being effected in a manner similar to that described for the fuel electrode.

While, for simplicity and clarity, the assembly described above comprises only a single fuel cell unit 5, 6, 7, 8, a plurality of such units may, as already mentioned be combined in series and/or parallel to form a battery.

The present invention will now be further illustrated with reference to the accompanying Examples of single fuel cell units made in accordance with the present invention. All of the Examples relate to a porous metal substrate in the form of a disc having a diameter of 2 in. To one face of the disc there was applied by the flame spraying process known as "Metco 404" a porous layer of nickel aluminide followed by a layer of solid state oxide, said oxide being applied by means of an electric plasma powder spray gun using an 80 volt/500 ampere arc in a mixture of nitrogen and hydrogen gases. A layer of silver of thickness 0.5 microns was then applied to the free face of the solid state oxide layer by vacuum evaporation, care being taken to ensure that no silver was deposited on the edge of the oxide layer. In the fuel cell units of

- Examples IV, VI, X, XII and XIII a bright platinum paint of the kind known as Johnson Matthey Bright Platinum G was applied to the layer of nickel aluminide immediately before application of the solid state oxide. The resulting fuel cell unit was then assembled between stainless steel end plates in the manner described above with reference to the accompanying drawings.
- 10 Comparison of Examples III with IV, V with VI, IX with X and XI with XII shows that an increase in output is obtained when, in accordance with the present invention, a porous layer of platinum is applied to the layer of nickel aluminide. From Examples III and VIII, and VII and IX, it is seen that an increase in output is obtained when zirconia stabilised with yttria is used in place of zirconia stabilised with lime as the solid electrolyte. The Examples also show that substantially higher outputs are obtained when stainless steel is used in place of nickel as the porous metal substrate.

Ex. No.	Porous Metal Substrate			Solid State Electrolyte		Thickness of Nickel Aluminate (In.)	Platinum Layer (0.5 Microns Thick)	Fuel	Operating Temp. (°C.)	Voltage	Output (milli-amps/sq. cm.)
	Nature	Thickness (In.)	Approx. Pore Size (Microns)	Nature	Thickness (In.)						
I	Roll compacted sintered nickel	0.025	5	Zirconia stabilised with 6.4% wt. CaO (i.e. 13 mole % CaO)	0.007	0.0025	No	Hydrogen	710 800	0.4 0.4	21 50
II	Roll compacted sintered nickel	0.040	5	As for Ex. I	0.008	0.010— 0.015	No	Hydrogen	750	0.5	25
III	Perforated nickel	0.026	50	As for Ex. I	0.008	0.010— 0.015	No	Hydrogen	750	0.5	18
IV	Perforated nickel	0.026	50	As for Ex. I	0.008	0.010— 0.015	Yes	Hydrogen	750	0.5	27
V	Sintered nickel on perforated nickel base	0.031	50	As for Ex. I	0.008	0.010— 0.015	No	Hydrogen	750	0.5	22
VI	Sintered nickel on perforated nickel base	0.031	50	As for Ex. I	0.008	0.010— 0.015	Yes	Hydrogen	750	0.5	30

Ex. No.	Porous Metal Substrate			Solid State Electrolyte		Thickness of Nickel Aluminate (In.)	Platinum Layer (0.5 Microns Thick)	Fuel	Operating Temp. (°C.)	Voltage	Output (milli-amps/sq. cm.)
	Nature	Thickness (In.)	Approx. Pore Size (Microns)	Nature	Thickness (In.)						
VII	Sintered stainless steel	0.067	25	As for Ex. I	0.008	0.010—0.015	No	Hydrogen	750	0.5	43
VIII	Perforated nickel	0.026	50	Zirconia stabilised with 14% wt. Y_2O_3 (i.e. 8 mole % Y_2O_3)	0.008	0.010—0.015	No	Hydrogen	750	0.5	34
IX	Sintered stainless steel	0.067	25	As for Ex. VIII	0.008	0.010—0.015	No	Hydrogen	750	0.5	170
X	Sintered stainless steel	0.067	25	As for Ex. VIII	0.008	0.010—0.015	Yes	Hydrogen	750	0.5	195
XI	Stainless steel gauze	0.035	50—75	As for Ex. VIII	0.008	0.010—0.015	No	Hydrogen	750	0.5	170
XII	Stainless steel gauze	0.035	50—75	As for Ex. VIII	0.008	0.010—0.015	Yes	Hydrogen	750	0.5	180

Ex. No.	Porous Metal Substrate			Solid State Electrolyte		Thickness of Nickel Aluminate (In.)	Platinum Layer (0.5 Microns Thick)	Fuel	Operating Temp. (°C.)	Voltage	Output (milli-amps/sq. cm.)
	Nature	Thickness (In.)	Approx. Pore Size (Microns)	Nature	Thickness (In.)						
XIII	Stainless steel gauze	0.056	50—75	As for Ex. VIII	0.006	0.010—0.015	Yes	Hydrogen	750 800	0.5 0.6	230 300
XIV	Stainless steel gauze	0.056	50—75	As for Ex. VI	0.006	0.010—0.015	No	2:1 -vol./vol.-methanol vapour/steam	750	0.5	120
XV	Stainless steel gauze	0.035	50—75	As for Ex. VIII	0.008	0.010—0.015	No	3:1 -vol./vol.-methanol vapour/steam	750	0.5	120
XVI	Stainless steel gauze	0.035	50—75	As for Ex. VIII	0.008	0.010—0.015	No	Kerosine Vapour	750	0.5	80

WHAT WE CLAIM IS:—

1. A fuel cell unit comprising a porous metal substrate having applied to one surface thereof a porous layer of nickel aluminide followed by a layer of solid oxide electrolyte as hereinbefore defined and then by an oxygen permeable layer of conductive material.
2. A fuel cell unit according to claim 1 wherein the layer of oxygen permeable material comprises metals of Group IB of the Periodic Table or platinum, palladium, iridium, ruthenium or rhodium.
3. A fuel cell unit according to claim 2 wherein the layer of conductive material is a continuous layer of silver.
4. A fuel cell unit according to any one of the preceding claims wherein the solid oxide electrolyte is zirconia stabilised with lime or yttria.
5. A fuel cell unit according to claim 4 comprising lime in the range 10—15 mole, per cent.
6. A fuel cell unit according to claim 4 comprising yttria in the range 5—12 mole, per cent.
7. A fuel cell unit according to any one of the preceding claims comprising, between and in contact with the layer of nickel aluminide and the layer of solid oxide electrolyte, a porous layer of platinum.
8. A fuel cell unit as herein described with reference to any of the examples.
9. A fuel cell unit according to claim 1, substantially as herein described.
10. A method of constructing a fuel cell unit comprising applying to one surface of a porous metal substrate a porous layer of nickel aluminide followed by a layer of solid oxide electrolyte as hereinbefore defined and then by an oxygen permeable layer of conductive material.
11. A method according to claim 10 comprising applying the nickel aluminide by flame spraying.
12. A method according to claim 10 or claim 11 comprising applying the solid oxide electrolyte by plasma spraying.
13. A method according to any one of claims 10—12 comprising applying to the layer of nickel aluminide a porous layer of platinum.
14. A fuel cell unit made in accordance with any of claims 10—13.
15. A fuel cell comprising one or more fuel cell units as claimed in any one of the claims 1—9 and 14.
16. A fuel cell, substantially as herein described with reference to the accompanying drawings.

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